Revue Roumaine de Chimie, **2008**, *53*(11), 1065–1068

RADIATION-INDUCED PREPARATION OF GYPSUM/ POLY(METHYL ACRYLATE) COMPOSITES

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Received February 5, 2008

Gypsum/ poly(methyl acrylate) composites have been prepared based on natural gypsum and the monomer methyl acrylate by means of gamma irradiation. The conversion of polymerization was followed up with respect to the irradiation dose using thermogravimetric analyzer. The data show that the yield of polymerization increases with increasing the irradiation dose, and levels off at a dose around 3-4 kGy where a yield of 87-88% was achieved. A thermomechanical analyzer was used to determine the glass transition temperatures (*T*g) of the pure polymers and composites prepared at the same irradiation dose using two modes with alternative variable force and constant force. The *Tg* of the pure poly(methyl acrylate) and the polymer composite are around 18.5 ^{o} and 19.6 ^{o}C, respectively.

INTRODUCTION

Composite materials are used in building construction, in the automotive industry and in aerospace technology. Polymeric materials are virtually able to compete with conventional materials in most industrial fields. Polymers have contributed substantially to the development of better, cheaper and more functional products in the factory or the appliances, and in the recreation and leisure industries.

By incorporation of special fillers into a polymer matrix, desired composite properties could be achieved to suit various applications.[1] In the rubber industry, finely divided fillers have already been utilized to modify the polymer properties. Carbon black has been used for a long time.[2-3] Silicas are also used to modify polymeric materials.[4-6] Gypsum and alumina were also used as filler for preparing polymer composites.[7-9]

The present work reports the preparation of composites consisting of methyl acrylate and commercially available gypsum using gamma radiation.

RESULTS AND DISCUSSION

1. Thermogravimetry

Natural gypsum powder was used as it is, without drying, because it has been previously showed that there is no significant influence of drying of the powder on the polymerization conversion by preparing polymer/ gypsum/ composites. Furthermore, the polymerization yield using chemically pure calcium sulfate powder and natural gypsum powder seems to be very similar.[8]

Various mixtures of methyl acrylate and gypsum powder were exposed to different Gamma doses. Figure 1 shows the TGA thermograms of methyl acrylate/ gypsum/ composites, which are irradiated at different doses: 1, 1.5, and 2 kGy; the first step in the thermogram corresponds to the evaporation of the monomer and the humidity in the samples; the second step corresponds to the decomposition of the polymer. It can be seen that the first step decreases with increasing the irradiation dose due to the increase of the polymerization conversion. The yields of polymerization are represented in Figure (2) with respect to the irradiation dose. The polymerization conversion increases with increasing the irradiation dose, and levels off up a dose of ≈ 3-4 kGy, achieving a conversion of 87-88%. This can be explained by the fact that the radical concentration, which acts as initiator, increases with increasing the irradiation dose and thus the reaction conversion.

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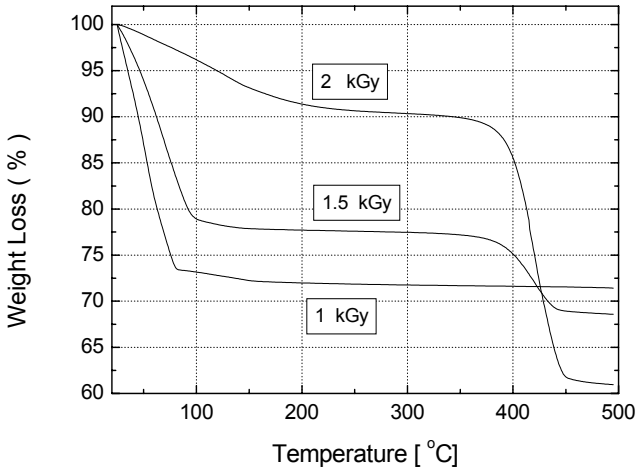

Fig. 1 – TGA thermograms of methyl acrylate/ gypsum/ composites for different preparation doses.

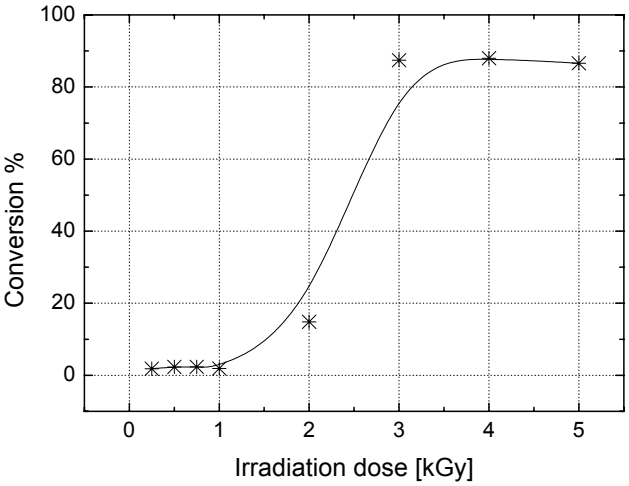

Fig. 2 – The yield of polymerization of methyl acrylate versus the irradiation dose for the methyl acrylate/ gypsum composites.

2. Glass Transition Temperature (T_g)

TMA spectrum has been recorded using an alternated force of 0.2 N in order to ensure that there is a real glass transition and to locate the T_g region as represented in Figure 3; it can be seen that the elongation increases significantly at the T_g region. TMA spectra with alternated force of 0.2 N were recorded for pure poly(methyl acrylate) and the polymer/ gypsum/ composite in order to compare their elasticity. The spectra showed that the elongation of poly (methyl acrylate)/ gypsum/ composite is significantly lower than that of pure polymer. This decrease is maybe due to reduced segmental mobility in the vicinity of the filler particulates.

TMA spectrum was recorded afterwards with constant force in order to determine the T_g; the T_g was then determined from this thermogram using the on-set method. The T_g of gypsum/ poly (methyl acrylate)/ composite is ≈ 19.6 °C. The T_g of the pure poly (methyl acrylate) was about 1 degree lower than that of the polymer composite. Differential scanning calorimetry (DSC) was also used to locate the glass transition temperature (T*g*) of the samples as represented in Figure 4. It can also be seen that the glass transition temperature of the poly (methyl acrylate)/ gypsum/ composites is slightly higher than the glass transition temperature of poly(methyl acrylate); $T_{on\text{-}set}$ and T_{mid} of pure poly (methyl acrylate) are 9.77 and 14.56 °C, respectively. $T_{on\text{-}set}$ and T_{mid} of poly(methyl acrylate)/ gypsum/ composites are 11.07 and 15.76 °C, respectively. This difference is most probably due to the interaction between the polymer matrix and filler particulates. Since the segmental mobility of the chains near the filler particles is reduced, the T_g of the composites

increases. In other composite systems, the increase of T_g has also been observed and documented; this behavior has been explained on the basis of reduced mobility of molecular segments in the vicinity of the filler particulates.[7]

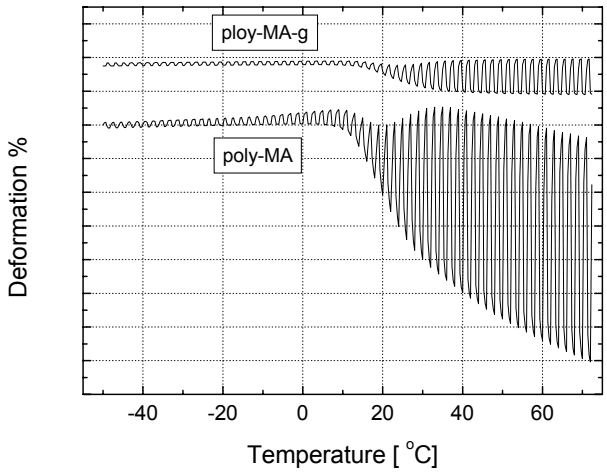

Fig. 3 – TMA spectrum with alternated force of 0.2 N for poly (methyl acrylate)/ gypsum/ composite irradiated at 5 kGy.

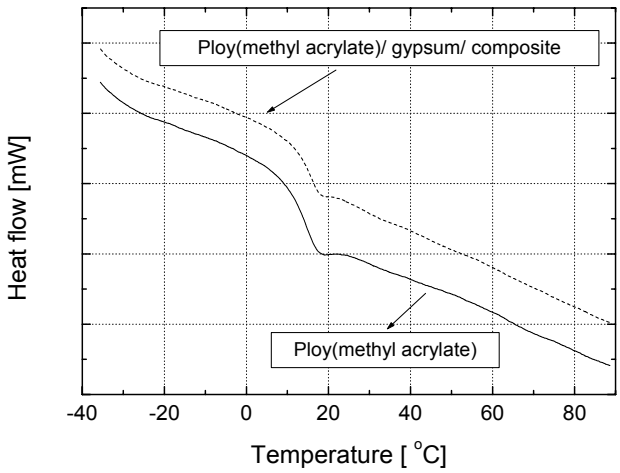

Fig. 4 – DSC spectra for pure poly (methyl acrylate) and poly (methyl acrylate)/ gypsum/ composite irradiated at 15 kGy.

EXPERIMENTAL

Natural gypsum powder was used, which is produced domestically from natural rocks in a mine near the city of Latakia in Syria. The sieved gypsum powder (0.3 meshes) was added to the liquid monomer step by step during stirring at room temperature that a weight ratio of 1:1 was achieved. The monomer/ gypsum/ mixtures were filled up in polyethylene ampoules, and then subjected to a ^{60}Co γ irradiator (Russian Gamma Cell, Type: Issledovatel); the irradiation was carried out at ambient temperature and a dose rate of around 3.5 kGy/h to different doses.

1. Thermogravimetric Measurements (TGA)

The dynamic weight loss tests were conducted using a Mettler instrument (TG50). The tests were carried out in a nitrogen atmosphere, purged (30 ml/ min) using sample weights of 10 - 15 mg at a heating rate of 10 °C / min. The resolution of the balance is given, as 1 microgram for weights less than 100 milligram, and the temperature precision of the instrument is ± 2 °C.

2. Thermomechanical Analysis (TMA)

TMA was used to locate the glass transition temperatures of the prepared samples. A Mettler equipment (TMA 40) was utilized in order to record the TMA spectra. The used instrument has a precision of ± 2 °C, and the total experimental errors in the measurements were estimated to be about ± 3 °C.

The PE container, used for the preparation of the samples, was removed and then sheets of ≈ 1 mm were cut, polished, and cleaned. TMA spectra were recorded in two modes. The first mode was using an alternated force in order to ensure that there is a real glass transition; alternated force between 0.1 and 0.2 N was applied in the most cases. The second mode was using a constant force of 0.1- 0.4 N, and the T_g was determined from these TMA thermograms using the on-set method.

3. Differential Scanning Calorimetry (DSC)

DSC was used to determine the glass transition temperatures of the prepared samples. A Mettler instrument (DSC20) was utilized to record the DSC spectra. All samples were tested in aluminum pans at a heating rate of 10 ^{o}C/ min over a temperature range from room temperature to 400 ^{o}C. The precision of the used instrument is ± 0.2 ^{o}C, and the experimental errors in the measurements were estimated to be about ± 0.5 ^{o}C.

CONCLUSION

Polymer/ Gypsum/ composites have been prepared based on natural gypsum powder and methyl acrylate by means of gamma irradiation. The conversion of polymerization was followed up with respect to the irradiation dose using a thermogravimetric analyzer. The data show that yield of polymerization increases with increasing the irradiation dose, and the highest yield obtained was around 87-88% by exposure of doses 3-4 kGy. Also the glass transition temperatures have been determined for the pure polymer and composites prepared at the same irradiation dose and have been found, to be 18.5 ^{o}C and 19.6 ^{o}C, respectively.

Acknowledgements: The author would like to thank Prof. I. Othman for his encouragement. He is also grateful to Mr's. M.K. Aljoumaa and M.A. Mougrabeya for their efforts during the experiments.

REFERENCES

1. H. Katz and J. V. Milewski (eds.), "Handbook of Fillers and Reinforcement for Plastics", Van Nostrand, New York, 1978.
2. Y. Huali, T. Hao, P. Jianhui, C. Xnfang, *Radiat. Phys. Chem.*, **1993**, *42*, 135-137.
3. N. A. Shaltout, M. M.Abou-Zeid, M. H: Moustafa and A. A.El-Miligy, *Arab-J. Nucl. Sci. Appl.*, **2002**, *35* (1), 25-35.
4. T.Çaykara and Güven O., *J. Appl. Polym. Sci.*, **1998**, *70* (5), 891-895.
5. T. Çaykara, M. S. Eroglu and O.Güven, *Polym. Degrad. Stabil.* , **1999**, *63*, 65-70.
6. T. Çaykara and O.Güven, *Europ. Polym. J.*, **1999**, *35*, 113-119.
7. T. Çaykara and O.Güven, *Polym. Comp.*, **1998**, *19*, 193-197.
8. Z.Ajji and H.Alkassiri, *Proceedings of the Symposium on Radiation Technology in Emerging Industrial Applications*, (IAEA TecDoc), **2003**, 41-45.
9. Z.Ajji, *Radiat. Phys. Chem.*, **2005**, *73*, 183-187.